Studies on the Corrosion of Tin. I : Corrosion in Hydrochloric Acid

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Synopsis

The corrosion testing of tin in hydrochloric acid solution was studied. At the beginning of this research, condition of making specimens was selected from the data of preliminary experiments and following experiments were carried out by using specimens prepared under that condition. (1) Relation between the corrosion rate of tin and concentration of hydrochloric acid solution. (2) Influence of stirring. (3) Influence of temperature rising. (4) Influence of addition of potassium bichromate, sodium nitrate, formaldehyde, sodium sulphite, stannous chloride and cuprous chloride on the corrosion rate of tin. (5) Corrosion velocity curve. And following facts were concluded from experiments: (1) Tin in hydrochloric acid shows the passive state at the acid concentration below 0.01 per cent. (2) The depolarizing corrosion increases with concentration from 0.01 to 3 per cent. (3) The depolarizing corrosion becomes complete at the concentration from 3 to 15 per cent. (4) The hydrogen evolution type of corrosion increases with the concentration from 15 to 25 per cent. (5) The hydrogen evolution type becomes complete at the concentration above 25 per cent.

I. Introduction

No systematic research on the corrosion of tin has been carried out. In order to clarify the corrosion mechanism and the resistance of it quantitatively, some experiments were done by the authors and the results with corrosion in hydrochloric acid solution are described in this paper.

II. Method of experiments

Chemical pure reagents were supplied for all experiments except for special cases described in those parts. Specimens were prepared from Katayama manufactured granular tin which was melted and cast in an iron mould and then cut in pieces of cylindrical shape in 5 mm in diameter and 20 mm in length without heat treatment; these were then wiped by a clean cloth containing benzol and stored for 1 week before testing. Corrosion experiments were done by the total immersion method, that is, 250 cc of corrosive was kept in a 450 cc capacity glass bottle and the specimen was suspended by a glass hook into the midst of the solution at room temperature except for special cases. Covers on the bottles were not used in general, but in corrosives having large vapor pressure or wet-absorbing power, the experiments were done in a covered bottle. Corrosion was

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estimated from weight decrease and observation of phenomenon, and the corrosion rate was shown in (weight decrease)/(initial weight)×100 per day, that is corrosion per cent per day.

III. Casting temperature

In order to determine the casting condition of a tin specimen, effects of casting temperature and mould temperature on corrosion of tin in 30 per cent of hydrochloric acid solution were tested for 1 day at room temperature.

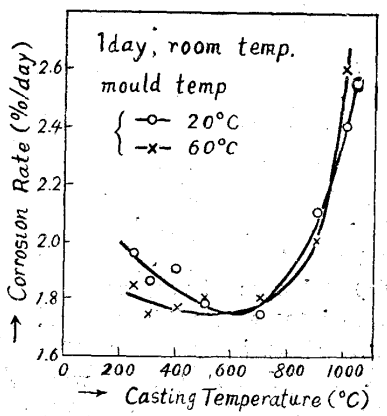

Fig. 1. Influences of casting temp. and mould temp. on corrosion in 30% HCl.

The results (Fig. 1) show that stable specimens are obtained from an ingot cast below 500° of melt into a mould heated at 60°. From the reason described above, all of the specimens were prepared from the ingot cast under the mentioned condition.

IV. Reproducibility

Corrosion rates of five specimens in 10 per cent of hydrochloric acid solution for 10 days at room temperature were compared with each other and the results obtained were as in Table 1.

Table 1. Reproducibility in 10% HCl. 10 days, room temp.

Specimen No.	1	2	3	4	5
Corrosion Rate (%/day)	0.0819	0.0822	0.0816	0.0820	0.0818

They show that the corrosion rate can be reproduced in 3 figures below decimal point. Corrosion rates, therefore, were calculated by 3 figures in this paper.

V. Corrosion rates vs. acid concentration

Corrosion rates of tin in various concentrations of hydrochloric acid solutions are shown in Figs. 2 and 3. Fig. 2 is the result tested for 1 day at room temperature and it shows that a depolarizing corrosion can be expected for corrosion in 5 to 20 per cent acid. Corrosion appearance also showed that hydrogen is evolved in acid above 25 per cent; Centnerszwer(1) observed the same phenomenon. Fig. 3 is the result tested in dilute acid for 10 days at room temperature. According to the figure, corrosion of tin begins at 0.05 per cent of acid and this coincides with results of measurement in electromotive forces by Brennert(2), who showed the critical point as pH 2. Appearances of specimens after corrosion are as follows: Specimens tested in acid below 0.01 per cent retain polished bright surfaces, in 0.05 to 3 per cent solutions they show corrosion

(1) M. Centnerszwer: Z. Phys. Chem., A 141 (1929), 167.
(2) S. Brennert: Int. Tin Res. Dev. Council, D-2 (1935).

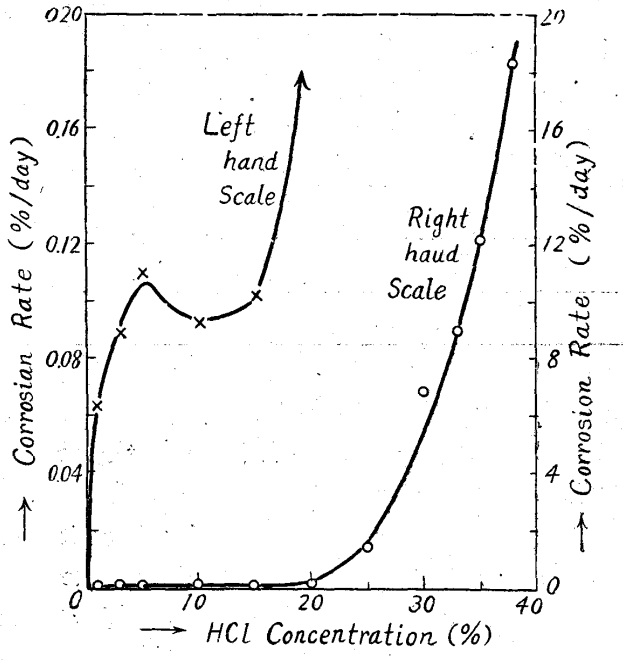

Fig. 2. Relation between corrosion and acid concentration. 1 day, room temp.

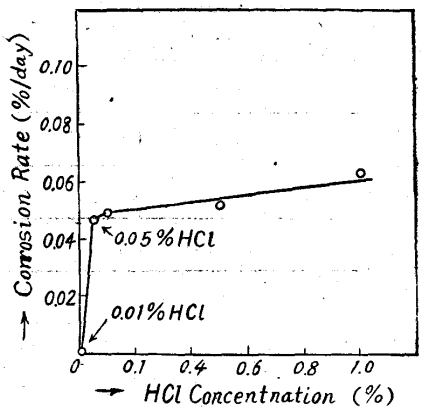

Fig. 3. Corrosion in dilute hydrochloric acid. 10 days. room temp.

spots in worm-eaten shape, in 5 to 20 per cent solutions crude soundy surfaces appear, and in 25 to 38 per cent solutions their crystal structure is exposed by corrosion.

Electrolytes are decomposed to ions in water and those ions effect water molecules by hydration. An important change in the nature of ions influenced by hydration is that the active force of ion is screened through a hydrated film. The reaction related with ions in water, therefore, are stimulated by the decreasing of hydration. According to Fig. 2, the reaction becomes active at 25 per cent acid which corresponds to ca. $HCl \cdot 6H_2O$. Since hydrogen ion in water goes to hydroxonium ion which combines with one water molecule, hydrogen chloride solution may becomes active at 25 per cent, provided that the hydration number of chlorine ion is 5. It has been beliebed that hydration of chlorine ion is 4.

VI. Influence of stirring

Influence of stirring on the corrosion of tin in hydrochloric acid solution was researched by the following method. A specimen was rotated at about 200 r. p. m. in corrosive for 50 hours at room temperature, and its weight decrease was compared with stagnant corrosion rate of tin under the same temperature and time.

Provided that the rate-determining step is a chemical reaction, the effect of stirring is comparatively small, but it is large in the case of diffusion control. According to Table 2, corrosion of tin in 10 per cent acid has a great effect of stirring and it shows that the corrosion velocity in 10 per cent acid is controlled by diffusion. In 30 per cent acid, the stirring effect is very small and this shows

that the corrosion in that acid is the case of activation control. Relative value in 20 per cent acid can be explained as the mixed form of both cases.

Table 2. Influence of stirring on corrosion. 50 hrs, room temp.

HCl Concentration (%)		10	20	30
Corrosion Rate (%/day)	Stirring	4.30	13.64	4.24
	Stagnant	0.210	2.13	3.47
Ratio Stirring/Stagnant		20.5	6.4	1.2

VII. Influence of temperature rising

For the sake of effect in temprise, corrosion vessels were held in a thermostat at 15° to 80°C (±2°) for 5 hours. The results obtained are shown in Fig. 4. Corrosion rates are shown by logarithmic scale, and the right hand scale is the one in 10 per cent and left is in 20 and 30 per cent acid.

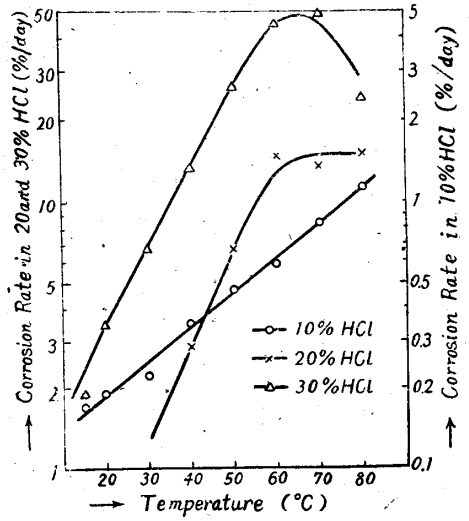

Fig. 4. Influence of temperature rising on corrosion in 10, 20 and 30% HCl. 5 hrs.

In the curves in Fig. 4, the following matters can be considered. Inclination of curve in 10 per cent acid is flattest and it shows that the corrosion rate is controlled by diffusion. Inclination in 20 per cent acid is near to that in 30 per cent, which corrosion is of the hydrogen evolution type. Corrosion in 20 per cent acid is the mixed type of depolarizing and hydrogen evolution at room temperature, but the latter mechanism becomes predominant with rising temperature.

In the case that a metal is corroding with hydrogen evolution, it can be said that the corrosion rate is great by the reason that the reaction between metal and corrosive is so vigorous as to be able to separate hydrogen and that the stirring of solution in the neighbourhood of the specimen is made by gas evolved and the corrosion product is spread into the outer part in the solution.

VIII. Influence of oxidizing agents

Fig. 5 is the result of corrosion testing of tin in 20 per cent hydrochloric acid solution containing oxidizing agents, sodium nitrate or potassium bichromate, for 10 days at room temperature. It may be expected that an addition of oxidizing agent accelerates corrosion and the amount of acceleration increases with increasing oxidizing power. Experiments showed that the effect of bichromate is greater than nitrate's. According to Watts and colleague(3), corrosion of tin

(3) Watts and Whipple: Mantell's Book "*Tin*" p. 304.

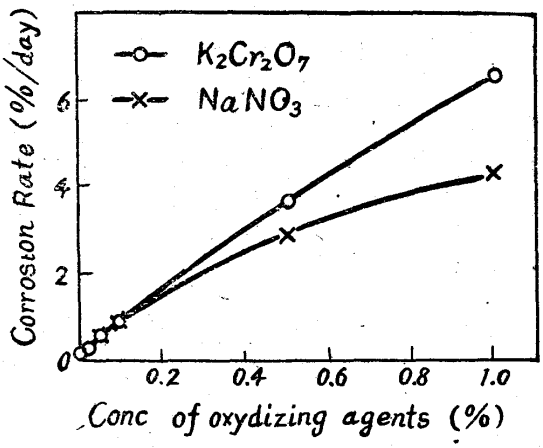

Fig. 5. Influence of oxidizing agents, $K_2Cr_2O_7$ and $NaNO_3$ in 20% HCl. 10 days, room temp.

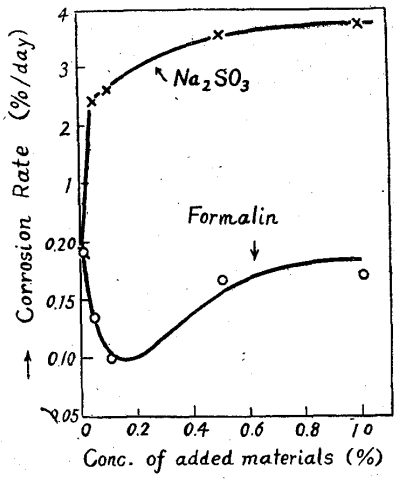

Fig. 6. Influence of formalin and Na_2SO_3 on corrosion in 20%HCl. 10 days, room temp.

in 1N-hydrochloric acid is accelerated as much as 40 times by the addition of 5 per cent of potassium permanganate and author's present experiment shows that the corrosion in 20 per cent acid is accelerated to 40 times by 1 per cent of potassium bichromate. When corrosion was made in acid containing more than 1 per cent of bichromate, chlorine gas was evolved.

IX. Influence of reducing agents

According to Prins(4), acid corrosion of tin is accelerated by the addition of benzaldehyde, but the present experiment shows that it is somewhat retarded by adding formaldehyde. Fig. 6 shows the result of corrosion test in 20 per cent hydrochloric acid solution containing formaldehyde (formalin liquor for medical use) for 10 days at room temperature.

Next, the same experiment was repeated by using sodium sulphite instead of formaldehyde. The result obtained (Fig. 6) shows that sodium sulphite does not act as a reducing agent, but act as an oxidizing agent. Sulphite ion depolarizes hydrogen on tin surface and alters to neutral sulphur or two negative valents of sulphur ion. The solution gave a smell of hydrogen sulphide with developing corrosion and powderish sulphur separated out on the specimen.

X. Influence of stannous ion

The influence of stannous ion on acid corrosion of tin was tested by the method described above and the results obtained are shown in Fig. 7, where stannous ion was added to 20 per cent hydrochloric acid as chloride and was calculated as $SnCl_2 \cdot 2H_2O$. Fig. 7 shows how stannous ion acts mild accelerater of corrosion and it can be understood as follows; stannous ion added to acid is oxidized by dissolved oxygen and it takes the form of stannic which behaves as a depolarizing agent on the surface of tin, that is stannous ion is a carrier of oxygen.

(4) Prins: Mantell's Book "*Tin*" p. 304.

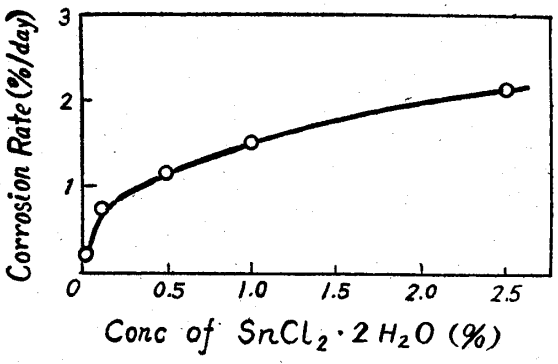

Fig. 7. Influence of Sn^{++} ion on corrosion in 20% HCl. 10 days, room temp.

Although the addition of stannous ion, therefore, corresponds to an addition of oxidizing agent apparently, its accelerating power is proportional to the oxygen solubility of solution and the effective amounts of stannous ion in a definite solution is of a definite value. Then, the addition of amounts of ion larger than that of effective value makes a potential difference between tin and solution noble and retards corrosion. If very large amounts of ion are added, corrosion is either completely retarded or in the intergranular type.

XI. Influence of cuprous ion

Corrosion rates measured in 20 per cent of hydrochloric acid solution containing cuprous chloride for 10 days at room temperature are shown in Fig. 8.

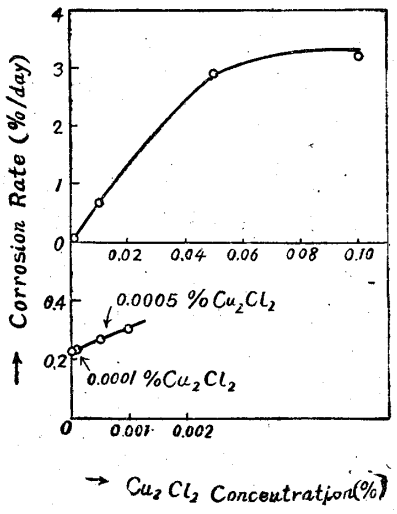

Fig. 8. Influence of Cu^{+} ion on corrosion in 20% HCl. 10 days, room temp.

Addition of cuprous ion in solution gives rise to exchange reaction between that ion and metallic tin, and it acts as an oxidizing agent. Since corrosion of tin in 20 per cent acid is the type mixed by depolarizing and hydrogen evolution, metallic copper separated out on the tin surface can become a cathodic nucleus for hydrogen evolution. Hydrogen evloution was observed at the later stage of corrosion experiment. Since cuprous ion added to solution acts as an oxidizing agent at the former stage it accelerates hydrogen evolution at the later stage, influence of cuprous ion on corrosion exceeds that of the oxidizing agent. According to Straumanis[5], dissolution of aluminium in 2N-hydrochloric acid is accelerated by an addition of 10^{-6} g of platinum ion and the present experiment shows that the corrosion of tin in 250 cc of 20 per cent acid is accelerated by 3×10^{-6} g cuprous ion.

XII. Corrosion velocity

The corrosion velocity curve shown in Fig. 9 was measured by following method. Five specimens were immersed at the same time in corrosives at room temperature and each specimen was taken out after 10 minutes, 1 hour, 5 hours, 1 day and 10 days respectively, and then weighed. Strictly speaking, since

(5) M. Straumanis and J. Bormanis: Korr. u. Metalls, 14 (1938), 1.

Table 3. Comparison between initial and later corrosion rate.

Time	10%HCl	20%HCl	30%HCl
10 mins	1.00	1.46	2.05
1 hr	1.00	1.02	4.66
5 hrs	1.00	1.11	27.4
1 day	1.00	2.25	37.3
10 days	1.00	4.68	17.9

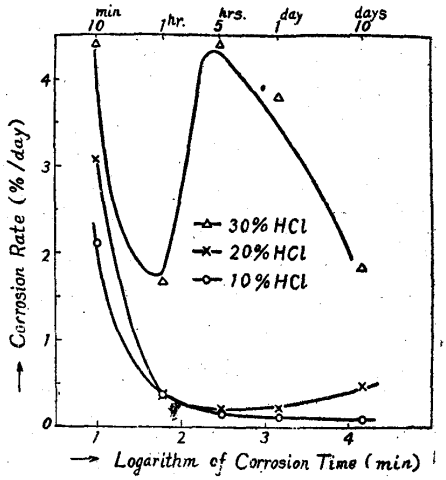

Fig. 9. Corrosion velocity curves, room temp.

corrosion velocity in the figure is demonstrated by the mean velocity during the time from immersion to taking out of the specimen, it may be considered that the curve shown in Fig. 9 is more lenient than the true velocity. According to the figure, the initial corrosion velocity is large and the differences between them are less than that of the later stage; for example, the velocity values in 20 and 30 per cent acid at each time when the velocity in 10 per cent acid is taken as a unit are shown in Table 3. In the curve for 30 per cent acid (Fig. 9), the corrosion velocity vigorously lowers and then rises again after 1 hour, until it reaches a maximum velocity after 5 hours. The outer layer of the specimen surface was dissolved out and the crystal grains were exposed after 5 hours in 30 per cent acid. It may be cansidered that the maximum of the velocity curve is due to an action of local cell produced between the inner part and boundary of the crystal. In 20 per cent acid, the local cell action is seen only at the later stage of corrosion. Corrosion velocity curve in 10 per cent acid shows a simple decreasing trend and it may be endorsed that the corrosion in 10 per cent acid is of a complete depolarizing type.

Summary

Corrosion of tin in hydrochloric acid can be classified as follows: (1) Tin in hydrochloric acid shows the passive state at the acid concentration below 0.01 per cent. (2) The depolarizing corrosion increases with concentration from 0.01 to 3 per cent. (3) The depolarizing corrosion becomes complete at the concentration from 3 to 15 per cent. (4) The hydrogen evolution type of corrosion increases with the concentration from 15 to 25 per cent. (5) The hydrogen evolution type becomes complete at the cencentration above 25 per cent.

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